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THE EQUILIBRIUM BETWEEN ACIDS AND BASES IN  
SEA WATER

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The alkaline reaction of sea water and the chemical equilibria that define it concern not only the oceanographer but also the geologist and the biologist. For information upon this subject must lead to further knowledge regarding geographical variations in the composition of the sea, the chemical reactions which have taken place during the existence of the ocean, the present movements of carbonic acid upon the earth, and the environmental relations of sea water to marine flora and fauna.

In the present investigation it has been sought, first, to determine the influence of carbon dioxide tension and of salinity upon the hydrogen ion concentration of sea water and, secondly, to construct a solution of exactly known composition, which shall reproduce the behavior of sea water when subjected to changes in carbonic acid concentration. This task has been accomplished with such accuracy as existing methods of investigation afford. The results define the acid-base relation between marine organisms and their environment, the fluctuations in this relationship, and the means by which such fluctuations are controlled. They also yield evidence concerning the geological history of the ocean. When combined with the observations of Palitzsch, they lead to a general description of the geographical variation in the chemical equilibria of sea water and to information concerning the gradients along which carbon dioxide is at present moving in the sea and in the air.

1. *Hydrogen Ion Concentration and Carbon Dioxide Tension of Sea Water.*—A large number of estimations of the hydrogen ion concentration of sea water, when saturated with carbon dioxide at tensions between 0 and 760 mm., have been made. The hydrogen ion concentrations were determined colorimetrically, following exactly the procedure of Palitzsch,<sup>1</sup> and at first with his kind assistance,<sup>2</sup> so that the results are strictly comparable with his. The standard solutions were in all cases analyzed with the hydrogen electrode. Carbon dioxide tensions, after equilibrium had been established, were determined either by chemical analysis of the gas phase or with the manometer. The following table corresponds to the curve which best fits the data of these experiments.

Salinity per cent	Temperature degrees	Hydrogen ion concentration	CO <sub>2</sub> tension mm.
31.92	20 ± 1	135 × 10 <sup>-7</sup>	760
31.92	20 ± 1	121 × 10 <sup>-7</sup>	700
31.92	20 ± 1	112 × 10 <sup>-7</sup>	600
31.92	20 ± 1	93 × 10 <sup>-7</sup>	500
31.92	20 ± 1	76 × 10 <sup>-7</sup>	400
31.92	20 ± 1	55 × 10 <sup>-7</sup>	300
31.92	20 ± 1	36.2 × 10 <sup>-7</sup>	200
31.92	20 ± 1	17.0 × 10 <sup>-7</sup>	100
31.92	20 ± 1	12.1 × 10 <sup>-7</sup>	75
31.92	20 ± 1	8.7 × 10 <sup>-7</sup>	50
32.45	20 ± 1	5.24 × 10 <sup>-7</sup>	25
32.45	20 ± 1	2.19 × 10 <sup>-7</sup>	10
32.45	20 ± 1	1.74 × 10 <sup>-7</sup>	7.5
32.45	20 ± 1	1.20 × 10 <sup>-7</sup>	5.0
32.45	20 ± 1	0.66 × 10 <sup>-7</sup>	2.5
32.45	20 ± 1	0.27 × 10 <sup>-7</sup>	1.0
32.45	20 ± 1	0.195 × 10 <sup>-7</sup>	0.75
32.45	20 ± 1	0.121 × 10 <sup>-7</sup>	0.5
32.45	20 ± 1	0.078 × 10 <sup>-7</sup>	0.25
32.45	20 ± 1	0.057 × 10 <sup>-7</sup>	0.1

2. *Effect of Salinity upon the Hydrogen Ion Concentration of Sea Waters at the same Carbon Dioxide Tension.*—Such variations of salinity as occur in the sea, although they do not ordinarily sensibly affect the proportions of the several components, must obviously exert a certain influence upon the hydrogen ion concentration. The following data indicate approximately the magnitude of this effect.

Number	Depth	Salinity	CO <sub>2</sub> tension mm.	Hydrogen ion concentration
10313	20 meters	30.73	0.3	0.093 × 10 <sup>-7</sup>
10301		31.58	0.3	0.087 × 10 <sup>-7</sup>
10305		32.05	0.3	0.085 × 10 <sup>-7</sup>
10305		32.34	0.3	0.085 × 10 <sup>-7</sup>
1000	20 ft.	32.45	0.3	0.087 × 10 <sup>-7</sup>
10299	210 meters	33.62	0.3	0.081 × 10 <sup>-7</sup>
10304		34.16	0.3	0.083 × 10 <sup>-7</sup>
10288	225 meters	34.60	0.3	0.079 × 10 <sup>-7</sup>

3. *Effect of Temperature upon the Hydrogen Ion Concentration of Sea Water.*—A more important effect upon hydrogen ion concentration is exerted by the temperature. This depends, first, upon the change in the absorption coefficient of the gas with change of temperature and, secondly, upon a simultaneous change in the ionization constants of the several substances involved in the equilibrium. Certain observations upon the apparent hydrogen ion concentrations of sea water at different temperatures, to which no value as quantitative estimations can at

present be attached, illustrate the general character of this effect, which is dependent mainly upon the first factor mentioned above.

<i>Temperature degrees</i>	<i>Salinity</i>	<i>Hydrogen ion concentration</i>
0	32.45	$0.141 \times 10^{-7}$
10	32.45	$0.107 \times 10^{-7}$
20	32.45	$0.085 \times 10^{-7}$
30	32.45	$0.060 \times 10^{-7}$
40	32.45	$0.0446 \times 10^{-7}$

These measurements indicate that under ordinary circumstances, when unaffected by the products of metabolism or the constituents of river water, the reaction of the sea water is fully determined by (1) the tension of carbonic acid, (2) the concentration of water, or salinity, and (3) the temperature. This relationship suggests a method of determining the carbon dioxide tension of sea water, which will be published later.

4. *Hydrogen Ion Concentration of Natural and Artificial Sea Water.*—So far as the acid-base equilibrium is concerned, sea water may be exactly imitated by a system consisting only of water and sodium chloride together with carbonic acid, and boric or silicic acid, partly combined with alkali. Thus, if a solution be prepared containing

NaCl.....	35.0	g. per liter
Na <sub>2</sub> CO <sub>3</sub> .....	0.1035	g. per liter
H <sub>3</sub> BO <sub>3</sub> .....	0.0620	g. per liter
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .....	0.0253	g. per liter

and set up in series with sea water of salinity 32.45, the two systems, after saturation with carbon dioxide at *any* tension between 0 and 760 mm., will possess the same hydrogen ion concentration, as estimated by indicators. This result, however, in that it is comparative, eliminates all estimations of the acidity of the solution. And accordingly the most trustworthy result of the present investigation is proof of the equivalence, in respect to hydrogen ion concentration, of sea water with this artificial system containing boric acid in a concentration 0.0015 molal, carbonic acid in an amount determined by the tension of its gas, and a single base in a concentration 0.0022 molal, distributed between boric and carbonic acids.

It is now evident that the ocean, which, because of the presence of free carbonic acid, was originally acid, and which has been becoming more alkaline from the accumulation of basic material, is at present in an epoch where the growing alkalinity is checked by the *buffer* action of acids of approximately the strength of boric acid. These acids are prob-

ably chiefly silicic acid and boric acid, though the conversion of bicarbonates into carbonates is also of importance.

These buffers regulate the reaction of sea water at the present time in a manner quite similar to the way in which bicarbonates and phosphates regulate the reaction of blood. The principal effect of the products of metabolism upon sea water is defined by the data concerning variation in the carbon dioxide tension.

5. *Geographical Variation in Carbon Dioxide Tension.*—Taking account of the facts as stated above, certain conclusions regarding geographical variations in the composition of sea water may be deduced from Palitzsch's data.

First, the uniform increase in acidity of sea water with increase of depth, proves that the concentration of free carbonic acid everywhere varies in like manner. This may be illustrated by one example.

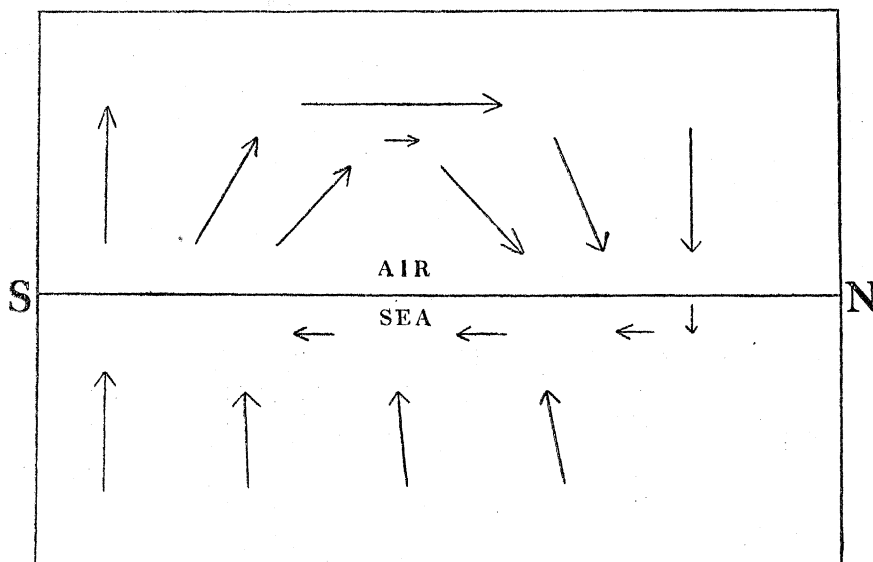
<i>Station 81.</i>				
<i>Depth meters</i>	<i>Temperature in situ</i>	<i>Salinity ‰</i>	<i>Hydrogen ion concentration at room temperature</i>	<i>Relative concentration of free carbonic acid</i>
0	17.94	35.43	$0.060 \times 10^{-7}$	1.0
50	13.56	35.52	$0.066 \times 10^{-7}$	1.3
100	12.56	35.63	$0.074 \times 10^{-7}$	1.8
400	11.01	35.57	$0.091 \times 10^{-7}$	2.5
800	11.25	36.02	$0.098 \times 10^{-7}$	2.8
1000	10.84	36.02	$0.098 \times 10^{-7}$	2.8
1200	9.89	36.00	$0.104 \times 10^{-7}$	3.1
1500	6.97	35.50	$0.112 \times 10^{-7}$	3.4
2000	4.20	35.10	$0.112 \times 10^{-7}$	3.4

Disregarding a conceivable effect of pressure, it seems to follow from these facts that, upon the whole, (i.e., in most places and at most seasons) carbonic acid is escaping from the sea into the air.

Secondly, the well marked variation in hydrogen ion concentration with latitude and therefore according to the temperature, in the case of surface waters, indicates that the concentration of free carbonic acid at the surface steadily increases in the direction of the pole. This, no doubt, depends upon the variation of the absorption coefficient of the gas with change in temperature. And, taking account of Krogh's<sup>3</sup> observations upon the high tensions of carbon dioxide, and the uniformly greater tension of atmospheric than of surface carbon dioxide in high latitudes, it appears to be certain that in cold marine regions carbonic acid is passing from air to sea. It does not appear likely that this absorption of carbon dioxide by the cold oceans can balance its escape from the warm oceans, first, because Palitzsch found, even in cold regions, an increase of hydrogen ion concentration with the depth, and,

secondly, because in the Mediterranean, where no deep arctic current flows, carbonic acid is escaping from the sea.

The special features of this movement of carbon dioxide can only be discovered through very extensive investigations, but its general character seems to be indicated by the following diagram.



MOVEMENTS OF CARBON DIOXIDE IN A VERTICAL NORTH-SOUTH PLANE, IN THE NORTHERN HEMISPHERE

These results afford one more instance of similarity between regulatory processes in the organism and in the environment.

We are greatly indebted to Dr. Palitzsch for furthering this investigation by his invaluable advice.

<sup>1</sup> Sven Palitzsch, Measurements of the hydrogen ion concentration in sea water, *Report on the Danish Oceanographical Expeditions 1908-10 to the Mediterranean and Adjacent Seas*, vol. 1, p. 237.

<sup>2</sup> During the early part of this investigation Dr. Palitzsch, as *Scandinavian Scholar*, was at work in the Gibbs Laboratory.

<sup>3</sup> August Krogh, The abnormal  $\text{CO}_2$  percentage in the air in Greenland and the general relations between atmospheric and oceanic carbonic acid, *Meddelelser om Grønland*, No. 25-26, p. 434, 1904.